Introduction: Ca-Al-rich inclusions (CAIs) in CV3 chondrites often display mass-dependent enrichments of the heavy isotopes of the more volatile elements, including Mg and Si, that are consistent with Rayleigh-type kinetic isotope fractionation during evaporation. Numerous laboratory studies of evaporation residues have been conducted to investigate isotope fractionation behavior during evaporation [1-3].

We have previously reported high-precision Mg isotopic data (obtained by multicollector inductively coupled plasma mass spectrometry) for a suite of Type B CAI-like silicate glasses evaporated in a vacuum furnace that clearly demonstrate Rayleigh fractionation behavior [4]. However, the kinetic gas-melt isotopic fractionation factors (α) indicated by these data differ markedly from the square root of the inverse mass ratio of the evaporating species (i.e., α = (24/25)^1/2, the value expected from kinetic theory if all isotopes of Mg have identical evaporation coefficients). Potential sources of error or bias, such as analytical artifacts, diffusion-limited evaporation and recondensation, have all been eliminated as possible causes of this discrepancy [5]. Thus, evaporation coefficients for the different isotopes of Mg do not appear to be identical, and they also appear to be weakly temperature dependent [6].

The discrepancy between expected and measured gas-melt isotope fractionation factors for Mg clearly demonstrates the need to determine these factors experimentally for other volatile elements. Here we report new ^29Si/^28Si isotope ratio data, measured by laser ablation multicollector ICPMS, on a subset of the samples that we have previously analyzed for Mg isotope compositions by solution techniques.

Experimental procedures and analytical methods: The sample materials analyzed were prepared from a starting material having a Type B CAI-like composition (approximately 46 wt.% SiO₂, 19 wt.% Al₂O₃, 12 wt.% MgO, 23 wt.% CaO) and were suspended in a vacuum furnace (P < 10^-6 torr) for periods of a few minutes to several hours. Additional experimental details may be found in [3]. All samples analyzed thus far had 6 mm initial diameters, are non-crystalline and were evaporated at 1800° C. The chemical composition of the starting material and evaporation run products were measured using a JEOL JSM-5800LV SEM with an Oxford Link ISIS-300 energy dispersive microanalysis system.

The Si isotope analyses we present were conducted in situ using a New Wave Research UP193HE excimer laser ablation system coupled to a Micromass IsoProbe multicollector ICPMS at The Field Museum. Spot sizes of 150 to 275 μm were used (depending on the Si content of the sample) and the laser was run at 5% relative power (equivalent to an energy density of ≈ 1.1 J/cm²) and a repetition rate of 4 Hz. Typical ion beam currents for ^28Si were 2 to 4 x 10^-11 A. Measurements were conducted in “soft extraction” mode (a small positive voltage is applied to the collimator cone) which lowers peak sensitivity by ≈50% but dramatically lowers background intensity. Si isotope measurements were performed by static multicollection, with each measurement consisting of twenty cycles of seven second integrations. Interferences on ^28Si and ^29Si were minor. ^14N²⁺ typically accounted for less than 0.5% of the ^28Si peak intensity and was subtracted by a 60 s on-peak gas blank measurement performed before each sample analysis. An organic species was present near the ^28Si peak, but had a slightly higher molecular mass (approximately 0.07 amu) that allowed interference-free measurements to be made on the low-mass side of the ^28Si peak top. Measurement of ^30Si was prevented by an isobaric interference from ^14N³O⁰, which could not be satisfactorily subtracted.

Analyses were conducted using the sample-standard bracketing technique. Glass chips made from the unevaporated starting material were used as bracketing standards. Reported data points represent the average of 3 to 5 individual measurements. Internal precisions for individual measurements are better than 0.7‰. External precisions, calculated from repeated measurements, are better than 0.4‰.

Results and discussion: The new silicon isotope data are plotted in Fig. 1. This log-log plot shows the fraction of ^28Si remaining in the residue (f) relative to that in the starting material versus R/R₀, the ^28Si/^28Si ratio in the evaporated sample normalized to that in the unevaporated starting material. All of the f values shown are calculated from molar Mg/Al ratios and assume no evaporative loss of Al. On Fig. 1, Rayleigh isotope fractionation lies along a straight line, with the slope given by 1-α. Although our current data set only
spans the range from 0 to 60% evaporative loss of Si, it defines a fairly tight correlation with a 1-\(\alpha\) slope of 0.0102\(\pm\)0.0004. This slope is very close to, but still distinguishably below, that of the “ideal” 1-\(\alpha\) value expected for Si evaporating as SiO (1-\(\alpha_{29Si/28Si} = 1 - (44/45)^{1/2} = 0.01117\)).

Also shown on Figure 1 is data from Wang et al. [2] who presented Mg, O and Si isotope data determined by ion probe (Mg) and gas source mass spectrometry (O and Si) on a suite of samples made from Si, Ti, Al, Fe, Mg and Ca oxides in solar proportions evaporated in vacuum at 1800° and 2000° C. The data of [2] are slightly more scattered and define a significantly lower 1-\(\alpha\) slope of 0.00861\(\pm\)0.00019. Similar data from Davis et al. [1] on forsterite evaporated at 1900° C (not shown) define an even shallower 1-\(\alpha\) slope of 0.00755 \(\pm\) 0.00005. The variation in 1-\(\alpha\) values for Si evaporation are significantly larger (relative to the “ideal” value) than that encountered for Mg evaporation over a similar range of sample compositions and run conditions (23.6% vs. 16.3%, respectively). This seems to indicate that \(\alpha_{Si}\) is more composition-dependent than \(\alpha_{Mg}\).

On a plot of Mg versus Si isotopic composition (Fig. 2) the samples studied here display an overall positive correlation, but with a pronounced curvature, indicating that the rate of Si isotope fractionation decreases relative to that of Mg as evaporation progresses. This is precisely what is expected for Rayleigh fractionation of this relatively Si-rich starting composition. The \(\delta^{29}Mg-\delta^{28}Si\) data fall on an isotope fractionation trajectory that corresponds to what is calculated using a thermodynamic model for the relative losses of Si and Mg together with the \(\alpha_{Si}\) value reported here and the 1800° C \(\alpha_{Mg}\) value from [6].


Figure 1. -ln\(f^{28}Si\) versus 1000 ln(R/R_0) for CAI vacuum evaporation residues measured by LA-MC-ICPMS. In this representation, Rayleigh fractionation results in data points that plot along straight lines whose slope is 1000(1-\(\alpha\)). Also, only 11 of the 15 data points of Wang et al. [2] fall within the range of this diagram.

Figure 2. \(\delta^{25}Mg\) versus \(\delta^{28}Si\) for the CAI evaporation residues superimposed on a calculated trajectory for Rayleigh fractionation assuming \(\alpha_{Mg} = 0.9864\) (from [6]) and \(\alpha_{Si} = 0.9898\) (from this study). \(\delta^{25}Mg\) data are from [4,5] and analytical uncertainties for \(\delta^{25}Mg\) are much smaller than the size of the symbols.